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BRIEF COMMUNICATION

Crystallographic Study of $YFe_2D_{3.5}$ by X-Ray and Neutron Powder Diffraction

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Crystallographic properties of $YFe_2D_{3.5}$ deuteride have been studied by X-ray and neutron powder diffraction. At 350 K, it crystallizes in the *R*-3*m* space group ($Z = 6$) with $a = 5.540(1)$ Å and $c = 13.568(2)$ Å. The location of deuterium atoms has been achieved in the paramagnetic state ($T = 350$ K). YFe_2 and $YFe_2D_{3.5}$ are ferromagnetic but deuterium absorption decreases the Curie temperature from 560 to 345 K. At room temperature, the neutron diffraction pattern of the deuteride exhibits a sharp rhombohedral distortion which is compared to that of the $ErFe_2D_x$ compound. © 1997 Academic Press

I. INTRODUCTION

YM_2 compounds (M = Mn, Co, Fe) crystallize in the C15 cubic structure and exhibit physical properties that are extensively studied. These compounds also absorb hydrogen involving structural and physical property modifications. Buschow *et al.* (1) reported that YFe_2 is ferromagnetic at room temperature (RT) and that it absorbs 3.6 H/f.u. involving a decrease in the Curie temperature. Recently, we observed (2) on YFe_2H_x that T_c rises from 560 K for $x = 0$ to 715 K for $2.2 \leq x \leq 2.7$ and decreases to 345 K for $x = 3.6$. For $x = 3.5$, the RT X-ray diffraction (XRD) pattern exhibits a splitting of the cubic lines involving a rhombohedral cell. Such distortion was already observed for RFe_2H_x (R = Er, Tb, Lu) (3–5). For the erbium compound, it was stated that the distortion appears for $x > 3.2$ H/f.u. but Park *et al.* (6) found that when H content is increased, the rhombohedral distortion becomes weaker and the structure returns to cubic for $ErFe_2H_{4.2}$. For Tb and Lu compounds, a similar evolution is observed but for $TbFe_2H_x$ the cubic to rhombohedral distortion occurs at lower H content ($x = 2.7$).

In this paper, we present XRD and neutron diffraction (ND) analysis on $YFe_2D_{3.5}$ deuteride below and above the magnetic transition. Structural distortion will be discussed and compared to that of the $ErFe_2D_x$ compound.

II. EXPERIMENTAL DETAILS

A. Synthesis

Preparation of a YFe_2 sample is described in (2). The homogeneity was checked by electron microprobe analysis which revealed few inclusions of yttrium oxide. X-ray analysis was performed on a PW1710 Philips diffractometer (Cu radiation) and gives a cubic cell parameter of $a = 7.355(1)$ Å. Weak additional lines belonging to Y_2O_3 were also observed. About 8 g of the alloy were ground under argon and sieved into powder. The deuteride was obtained by exposing the sample to deuterium at RT up to 3.5 D/f.u.. Due to the pressure gauge range, the pressure–composition isotherm (PCI) curve was not measured below 2 D/f.u.

B. Neutron Diffraction

ND measurements were performed on the 3T2 diffractometer at the Laboratoire Léon Brillouin in Saclay. The wavelength was 1.227 Å in the angular range $6° < 2\theta < 120°$ with steps of 0.05°. For the RT pattern, the sample holder was a silica tube under D_2 pressure whereas at 350 K it was an open vanadium can. From previous study (2), it is known that no significant desorption occurs below 410 K. Diffraction patterns were refined using the program FULLPROF (7).

III. RESULTS

YFe_2 absorbs 3.5(1) D/f.u. under 0.1 bar. Its equilibrium plateau pressure (Fig. 1) below 2 D/f.u. is estimated to be

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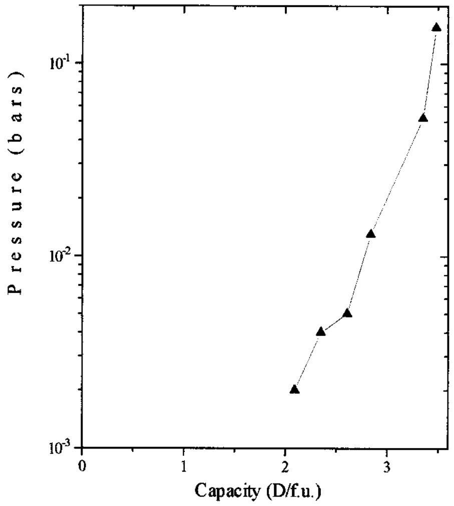

FIG. 1. Absorption pressure–composition isotherm of YFe_2 at 298 K.

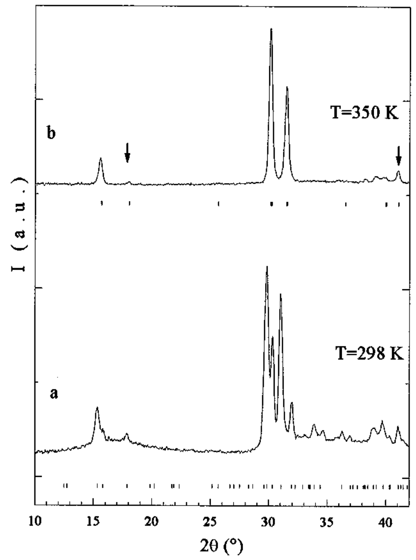

FIG. 2. $YFe_2D_{3.5}$ neutron diffraction patterns (a) at $T = 298$ K and (b) at $T = 350$ K (Arrows indicate the peaks which do not belong to the cubic cell at 350 K).

very low ($< 10^{-3}$ bar). From the XRD analysis at RT, which does not involve magnetic or deuterium contributions, we found a rhombohedral cell ($R1$) built on the primitive one from vectors $\mathbf{0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0}$ with $a = 5.508(1)$ Å and $\alpha = 61.4(1)°$. The structure was described in the $R\bar{3}m$ space group using the hexagonal description, $a = 5.627$ Å and $c = 13.344$ Å.

The neutron diffraction pattern of the deuteride (Fig. 2a) recorded at RT exhibits both splitting of the main lines and appearance of extra lines which cannot be indexed in the $R1$ cell. An attempt to index this pattern in a larger cell ($R4$) built on vectors **100**; **010**; **001** leads to $a = 11.249(1)$ Å and $c = 13.344(1)$ Å in hexagonal description. However, it was not possible to fully index this diagram even with this larger cell. At 350 K, above T_c, the deuteride exhibits a simpler neutron diffraction pattern (Fig. 2b) without the rhombohedral distortion observed at 298 K. However, careful examination of the pattern reveals (apart from some lines around $2\theta = 40°$ attributed to Y_2O_3) the presence of two weak extra lines (arrows in Fig. 2b) which cannot belong to the cubic cell. Therefore, the pattern was indexed in the $R\bar{3}m$ space group with cell parameters $a = 5.539(1)$ Å and $c = 13.568(2)$ Å ($\Delta V/V = 22\%$). No contraction along the 111 axis is observed since this hexagonal cell is equivalent to a cubic one with $a = 7.834$ Å. From our refinement (Table 1 and Fig. 3), the metallic atom positions are preserved in the deuteride. Concerning deuterium atoms, in the C15 phases, $A2B2$ tetrahedral sites are preferentially occupied. This $96g$ position ($Fd3m$) splits into two $18h$ and one $36i$ positions in the $R\bar{3}m$ space group. Occupancy factor refinement shows that only two sites are occupied ($36i$, 37%, and one $18h$, 45%). No evidence for occupation of $AB3$ or $B4$ sites was found. The total D content obtained from ND analysis (3.54(12) D/f.u.) is in good agreement with that measured from volumetric device. Tetrahedral site environments are described in Table 2.

IV. DISCUSSION

RM_2 Laves phase compounds absorb large amounts of hydrogen. However, for high concentration, structural

TABLE 1
Atomic Parameters from ND Data at 350 K for $YFe_2D_{3.5}$

Atoms	x	y	z	B	N
Y $6c$	0	0	0.1256(5)	1.033	1
Fe1 $3b$	0	0	1/2	0.627	1
Fe2 $9e$	1/2	0	0	1.946	1
D1 $18h$	0.8610(24)	2.x	0.2584(9)	1.79(15)	0.449(17)
D2 $36i$	0.2331(22)	0.3178(16)	0.4426(5)	1.79(15)	0.366(12)
Reliability factors (%)	$R_p = 6.50$ $R_{\omega p} = 7.35$	RI = 8.81 $R_{exp} = 2.98$	Cell par. (Å) S.G. $R\bar{3}m$	$a = 5.5399(4)$ $c = 13.5681$ (20)	D/f.u. = 3.54(12) $\Delta V/V = 22\%$

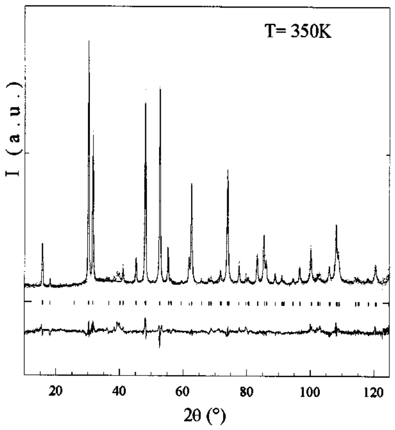

FIG. 3. Refined $YFe_2D_{3.5}$ neutron diffraction pattern recorded at 350 K. (Peak positions (|), observed (…), calculated (—), and difference (below) patterns.)

instabilities are observed. For example, $R_{1-x}Ni_2H_y$ hydrides become amorphous for $y > 2.7$ H/f.u In a previous paper (8), we attributed this behavior to strains related to the presence of vacancies in the intermetallic compound itself. For lighter transition metals (M = Mn, Fe), no vacancies are observed in the intermetallic compounds and the hydrides remain crystallized but structural distortions are commonly observed (3–5, 9).

From magnetic study (2) it is known that $YFe_2D_{3.5}$ orders ferromagnetically below $T_c = 345$ K. At 350 K, in the paramagnetic state, the neutron diffraction exhibits a rhombohedral structure without contraction along the 111 axis. The symmetry lowering is related to deuterium ordering since only two of the three available $A2B2$ sites are occupied.

At RT, $YFe_2D_{3.5}$ is ordered in a ferromagnetic state and a sharp rhombohedral distortion involving the contraction of the 111 axis occurs. The structure can be no longer described in the high temperature $R1$ cell and exhibits splitting of the main lines and superstructure lines. As previously measured (2), the transition is related to magnetic ordering with $T_c \approx 345$ K and the structural transformation is due to magnetostriction effects. This is supported by previous works (10) which reports on magnetoelastic distortion in a rare earth–iron intermetallic Laves phase.

TABLE 2
D Site Environments for $YFe_2D_{3.5}$ at 350 K

D atoms	Environment (± 0.02 Å)			Site radius (± 0.01Å)	Occupancies % (%)
D1 18*h*	1	Y	2.24	0.43	45(2)
	1	Y	1.99		
	2	Fe2	1.80		
D2 36*i*	1	Y	2.37	0.43	37(1)
	1	Y	2.18		
	1	Fe1	1.76		
	1	Fe2	1.54		

Note. The atomic radii use for calculations of the site radius were 1.78 and 1.26 Å for Y and Fe atoms, respectively.

Such rhombohedral distortion has been already observed for RM_2 hydrides with large D content. $ErFe_2H_x$ exhibits a rhombohedral symmetry for $x = 3.3$ D/f.u. which was attributed to occupancy of $AB3$ sites (4). However, in the present work, above T_c, only $A2B2$ tetrahedral sites are occupied and there is no evidence for $AB3$ occupancy. Therefore, the rhombohedral distortion is attributed to magnetic effects.

Same effects are also expected for $ErFe_2H_{3.3}$ since at RT, the hydride is in a magnetically ordered state. For larger H content ($x = 3.9$), Gualtieri *et al.* (11) report a cubic structure at RT whereas T_c is decreased down to 280 K. In fact, several authors (12, 13) report the recovering of the cubic structure in the paramagnetic state. However, some deuterium ordering is already observed very close to T_c. This effect can also be involved in the distortion. Such competition between deuterium and magnetic orderings is commonly observed in intermetallic hydrides (14) and both phenomena seem to be correlated.

V. CONCLUSION

We conclude that the compound $YFe_2D_{3.5}$ is cubic in the paramagnetic state and that a rhombohedral distortion appears below T_c due to magnetostriction effects involving both cell contraction and further deuterium ordering. However, it was not possible from powder diffraction data to determine both nuclear and magnetic structures at RT. A systematic study with scanning of the temperature when recording diffraction patterns will be helpful for a better understanding of the structural transition observed in this compound.

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